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# Reflection absorption infrared spectroscopy and temperature programmed desorption investigations of the interaction of methanol with a graphite surface

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Reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD) have been used to investigate the adsorption of methanol ( $\text{CH}_3\text{OH}$ ) on the highly oriented pyrolytic graphite (HOPG) surface. RAIRS shows that  $\text{CH}_3\text{OH}$  is physisorbed at all exposures and that crystalline  $\text{CH}_3\text{OH}$  can be formed, provided that the surface temperature and coverage are high enough. It is not possible to distinguish  $\text{CH}_3\text{OH}$  that is closely associated with the HOPG surface from  $\text{CH}_3\text{OH}$  adsorbed in multilayers using RAIRS. In contrast, TPD data show three peaks for the desorption of  $\text{CH}_3\text{OH}$ . Initial adsorption leads to the observation of a peak assigned to the desorption of a monolayer. Subsequent adsorption leads to the formation of multilayers on the surface and two TPD peaks are observed which can be assigned to the desorption of multilayer  $\text{CH}_3\text{OH}$ . The first of these shows a fractional order desorption, assigned to the presence of hydrogen bonding in the overlayer. The higher temperature multilayer desorption peak is only observed following very high exposures of  $\text{CH}_3\text{OH}$  to the surface and can be assigned to the desorption of crystalline  $\text{CH}_3\text{OH}$ . © 2005 American Institute of Physics. [DOI: 10.1063/1.1839554]

## I. INTRODUCTION

Methanol ( $\text{CH}_3\text{OH}$ ) is found in the interstellar medium (ISM) in the form of interstellar ices, frozen out on the surface of dust grains.<sup>1</sup> It is widely thought that the majority of the  $\text{CH}_3\text{OH}$  present in these ices does not form in the gas phase and subsequently accrete on the surface of the grains. Instead it is hypothesized that  $\text{CH}_3\text{OH}$  forms directly on the surface of the dust, as a result of the successive heterogeneous hydrogenation of  $\text{CO}$ .<sup>2,3</sup> With this in mind, we have used reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD) to investigate the adsorption of  $\text{CH}_3\text{OH}$  on, and its desorption from, a highly oriented pyrolytic graphite (HOPG) surface held at around 100 K. This investigation forms part of a wider study of the mechanism of formation of  $\text{CH}_3\text{OH}$  on dust grain analog surfaces.

Dust grains in the ISM are thought to consist mainly of carbonaceous and siliceous material and are often covered in films of ice.<sup>1</sup> HOPG, and other carbon based surfaces, can be considered suitable analogs of dust grains and have been used previously in investigations of  $\text{H}_2$  formation on dust grains.<sup>4–7</sup> The temperature in the ISM, where these ice covered grains are found, is around 10–20 K. Although the experiments described here are not undertaken at this temperature, they still allow an understanding of the interaction of  $\text{CH}_3\text{OH}$  with the HOPG surface to be gained.

The only previous investigation of  $\text{CH}_3\text{OH}$  adsorption on HOPG was performed by Wang *et al.*<sup>8</sup> using atomic force microscopy. This study showed physisorbed multilayer

growth of  $\text{CH}_3\text{OH}$  on HOPG. Irregular islands of  $\text{CH}_3\text{OH}$  were observed and it was possible to distinguish between  $\text{CH}_3\text{OH}$  adsorbed in a bilayer and in a multilayer.

In contrast, the interaction of  $\text{CH}_3\text{OH}$  with metal surfaces has been widely studied due to its widespread application in elementary catalytic processes<sup>9</sup> and in fuel cells.<sup>10,11</sup> The adsorption and reaction of  $\text{CH}_3\text{OH}$  with metal surfaces have been discussed in several review articles.<sup>12–14</sup>  $\text{CH}_3\text{OH}$  has been shown to decompose to form methoxy ( $\text{H}_3\text{CO}-$ ) on most metal surfaces<sup>12,15–29</sup> and the decomposition can be promoted by coadsorbed oxygen, particularly on Au, Ag, and Cu surfaces.<sup>20,21,27,30,31</sup> At lower temperatures, physisorbed multilayers of  $\text{CH}_3\text{OH}$  are observed, adsorbed on top of the underlying chemisorbed layer.<sup>15–17,19,21–25,27,29,32–35</sup>

A detailed RAIRS and TPD study of the adsorption of  $\text{CH}_3\text{OH}$  on  $\text{Pd}\{110\}$  at 124 K was performed by Pratt and co-workers.<sup>15</sup> Initial adsorption of  $\text{CH}_3\text{OH}$  led to the formation of a chemisorbed layer. Further adsorption then led to the formation of a multilayer. RAIRS was used to show that the multilayer consisted of a crystalline structure in which hydrogen bonded chains of molecules were formed.<sup>15</sup> In addition to the crystalline multilayer, a “sandwich” layer was also identified on  $\text{Pd}\{110\}$ <sup>15</sup> which had a different RAIRS spectrum to both the multilayer and the chemisorbed monolayer. The formation of crystalline multilayers has also been observed for  $\text{CH}_3\text{OH}$  adsorbed on  $\text{Ru}\{001\}$ ,<sup>25</sup> polycrystalline Pt,<sup>32</sup>  $\text{Pt}\{111\}$ ,<sup>34</sup>  $\text{Rh}\{100\}$ ,<sup>28</sup>  $\text{Pd}\{100\}$ ,<sup>22</sup> and  $\text{Cu}\{110\}$ .<sup>35</sup> In all cases, formation of the crystalline phase was temperature dependant and could only be observed following a certain minimum exposure of  $\text{CH}_3\text{OH}$ . The formation of a crys-

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talline multilayer was characterized by the observation of splitting in the O–H region of the infrared spectrum, with bands being observed at 3301 and 3193  $\text{cm}^{-1}$ .<sup>15,34</sup>

TPD studies of the desorption of  $\text{CH}_3\text{OH}$  from a range of metal surfaces have also been performed. Pratt and co-workers<sup>15</sup> observed two main peaks in the TPD spectrum for  $\text{CH}_3\text{OH}$  adsorbed on  $\text{Pd}\{110\}$  at 143 and 230 K. The lower temperature peak did not saturate and was assigned to physisorbed  $\text{CH}_3\text{OH}$ , while the higher temperature peak was assigned to the desorption of chemisorbed  $\text{CH}_3\text{OH}$ .<sup>15</sup> This TPD spectrum was in broad agreement with those observed for  $\text{CH}_3\text{OH}$  desorption from other metal surfaces.<sup>22,25,28,32,35</sup> However, a TPD study of  $\text{CH}_3\text{OH}$  desorption from  $\text{Ag}\{111\}$  showed three desorption features.<sup>33</sup> The highest temperature peak was assigned to the desorption of the monolayer. The two lower temperature peaks were assigned to the desorption of the multilayer, with the higher of the two peaks being assigned to amorphous  $\text{CH}_3\text{OH}$  desorption and the lower of the two peaks assigned to the desorption of crystalline  $\text{CH}_3\text{OH}$ .<sup>33</sup> This is in disagreement with the TPD data for desorption of  $\text{CH}_3\text{OH}$  from  $\text{Pd}\{110\}$ , where Pratt, Escott, and King<sup>15</sup> indicate that they could not distinguish the crystalline and amorphous  $\text{CH}_3\text{OH}$  phases during desorption.

Several authors<sup>22,36</sup> have noted that multilayer desorption peaks, observed in the TPD for increasing exposures of  $\text{CH}_3\text{OH}$  to the surface, do not share a leading edge as would be expected for zero order desorption. This suggests that multilayer desorption is fractional order, and has previously been attributed to the formation of hydrogen bonds in the physisorbed layer.<sup>22,36</sup> Further evidence for the strong influence of hydrogen bonding on  $\text{CH}_3\text{OH}$  adsorption comes from the observation that occupation of the multilayer is often observed even before the monolayer is saturated.<sup>15,28,36</sup>

Here we describe detailed RAIRS and TPD investigations of the adsorption of  $\text{CH}_3\text{OH}$  on HOPG at both 100 and 130 K. The latter temperature was chosen as it is close to the temperature at which the amorphous to crystalline transition is observed for solid  $\text{CH}_3\text{OH}$ .<sup>34</sup>

## II. METHODOLOGY

Experiments were performed in an ultrahigh vacuum (UHV) chamber that has a base pressure of  $\leq 2 \times 10^{-10}$  mbar. The HOPG sample was purchased from Goodfellows Ltd. and was cleaved prior to installation in the UHV chamber using the “Scotch tape” method. The sample was cleaned before each experiment by annealing at 500 K in UHV for 3 min. Sample cleanliness was confirmed by the absence of any desorbing species during TPD experiments performed with no dosage. The sample was cooled to  $\sim 100$  K by pouring liquid nitrogen down the cold finger on which the sample was mounted.  $\text{CH}_3\text{OH}$  (99.9% purity, BDH Laboratory Supplies Ltd.) was admitted into the chamber by means of a high precision leak valve and the purity was checked with a quadrupole mass spectrometer before each experiment. All exposures are measured in Langmuir (L), where 1 L =  $10^{-6}$  mbar s.

RAIR spectra were recorded using a Mattson instruments RS1 research series Fourier transform infrared spectrometer coupled to a liquid nitrogen cooled mercury cad-

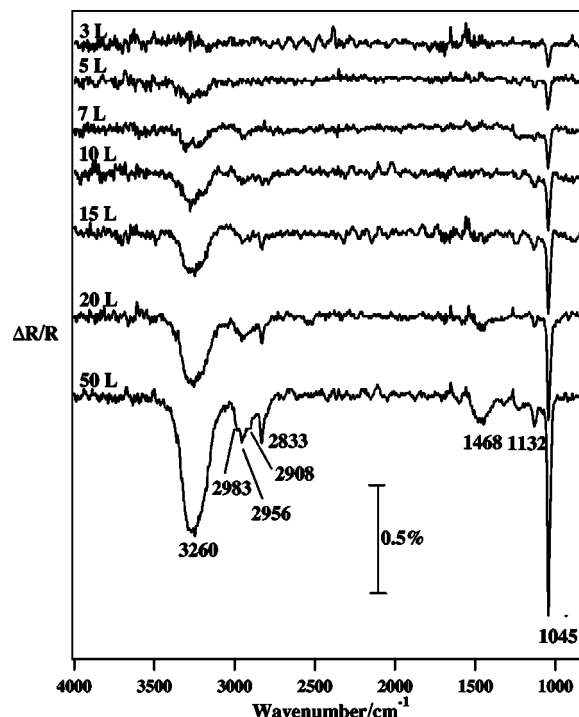


FIG. 1. RAIR spectra recorded following the adsorption of  $\text{CH}_3\text{OH}$  on HOPG at 97 K. The given exposures are marked on the figure.

mium telluride (MCT) detector. All spectra were taken at a resolution of 4  $\text{cm}^{-1}$  and are the result of the coaddition of 256 scans, taking  $\approx 3$  min to collect each spectrum. In RAIRS experiments where the sample was heated, it was annealed to a predetermined temperature, held at this temperature for 3 min, and then cooled back down to the base temperature before a spectrum was recorded. TPD spectra were recorded with a Hiden Analytical HAL201 quadrupole mass spectrometer. All spectra were recorded at a heating rate of 0.5  $\text{K s}^{-1}$ .

## III. RESULTS AND DISCUSSION

### A. RAIRS experiments

RAIR spectra recorded following  $\text{CH}_3\text{OH}$  adsorption on HOPG at 97 K are shown in Fig. 1. Initial exposure of the surface to  $\text{CH}_3\text{OH}$  leads to the appearance of one band at 1045  $\text{cm}^{-1}$ . With increasing exposure, this band increases in intensity, but does not shift in frequency. Following a 5 L exposure of  $\text{CH}_3\text{OH}$  a broad band, centered at 3260  $\text{cm}^{-1}$ , also grows into the spectrum. Similar to the band at 1045  $\text{cm}^{-1}$ , this band grows in intensity with increasing exposure but does not undergo a frequency shift. As the  $\text{CH}_3\text{OH}$  exposure is increased to 7 L and above, additional bands at 1132, 1468, 2833, 2908, 2956, and 2983  $\text{cm}^{-1}$  also grow into the spectra seen in Fig. 1. Increasing the exposure further (up to a total of 300 L) increases the intensity of these bands but does not lead to the observation of any additional spectral features. It is not possible to saturate any of these bands with increasing exposure, indicating that they are due to the formation of physisorbed multilayers of  $\text{CH}_3\text{OH}$  on the HOPG surface.

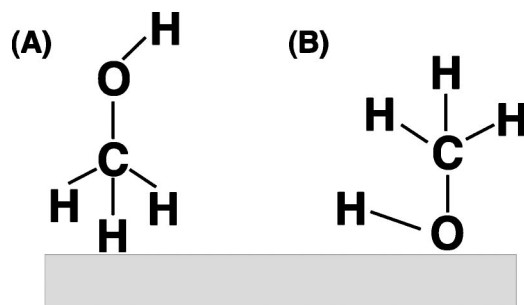


FIG. 2. Possible orientations of  $\text{CH}_3\text{OH}$  adsorbed on HOPG in the monolayer regime. The most likely orientation is that shown in (b) where the O atom of the  $\text{CH}_3\text{OH}$  bonds closest to the surface.

It is clear from the spectra in Fig. 1 that chemisorbed  $\text{CH}_3\text{OH}$  is not formed on HOPG. However, at lower exposures ( $\leq 7$  L) it is assumed that the  $\text{CH}_3\text{OH}$  is adsorbed on the HOPG surface in a monolayer, although it is not possible to distinguish between monolayer and multilayer adsorption in the RAIR spectra. TPD spectra (shown later) do show a clear difference between first layer (monolayer)  $\text{CH}_3\text{OH}$  and subsequent multilayer  $\text{CH}_3\text{OH}$ . The bands observed in the RAIR spectrum of the monolayer, at 1045 and  $3260\text{ cm}^{-1}$ , can be assigned by comparison with previous data for  $\text{CH}_3\text{OH}$  adsorbed on metal surfaces<sup>15–17,19,21–25,27,29,32–35</sup> and in an Ar matrix.<sup>37</sup> The bands are assigned to the symmetric C–O stretch and symmetric O–H stretch of  $\text{CH}_3\text{OH}$ , respectively. Since these bands are not shifted, compared to those

seen for higher exposures of  $\text{CH}_3\text{OH}$  (Fig. 1), it is assumed that the monolayer is physisorbed on the HOPG surface.

The data shown in Fig. 1 for low exposures give an indication of the orientation of the first few layers of  $\text{CH}_3\text{OH}$  adsorbed on the HOPG surface. The selection rules imposed by RAIRS on a metal surface also hold for adsorption on HOPG<sup>38</sup> and state that only vibrational modes with a component of the dipole moment perpendicular to the surface can be observed. Figure 1 shows that, at low exposures, only the C–O stretch of  $\text{CH}_3\text{OH}$  is observed, suggesting that the O–H stretch is lying parallel to the surface as shown in Fig. 2. It is most likely that  $\text{CH}_3\text{OH}$  bonds to the surface via its O atom as shown in Fig. 2(b), in agreement with previous observations on other surfaces.<sup>36</sup>

As already discussed, higher exposures of  $\text{CH}_3\text{OH}$  on HOPG lead to the formation of multilayers on the surface, and the bands observed in the RAIR spectra in Fig. 1 are in good agreement with those observed for multilayer  $\text{CH}_3\text{OH}$  on a number of metal surfaces.<sup>15–17,19,21–25,27,29,32–35</sup> Table I shows the assignment of the vibrational bands observed in Fig. 1 for the adsorption of  $\text{CH}_3\text{OH}$  on the HOPG surface. Included for comparison are band assignments for multilayer  $\text{CH}_3\text{OH}$  adsorbed on  $\text{Pd}\{110\}$ <sup>15</sup> and  $\text{Rh}\{100\}$ ,<sup>28</sup>  $\text{CH}_3\text{OH}$  contained in an Ar matrix<sup>37</sup> and crystalline  $\text{CH}_3\text{OH}$ .<sup>39</sup>

The  $\text{CH}_3\text{OH}$  multilayer formed on HOPG exhibits very strong intermolecular hydrogen bonding, as demonstrated by the broadness of the O–H stretch at  $3260\text{ cm}^{-1}$ . In addition, the O–H stretch is down shifted by  $\sim 400\text{ cm}^{-1}$  from the gas

TABLE I. Table showing the assignment of the vibrational bands observed for  $\text{CH}_3\text{OH}$  adsorbed on the HOPG surface at 97 K (Fig. 1). Also included is an assignment of the bands observed when an overlayer of  $\text{CH}_3\text{OH}$ , adsorbed at 97 K, is annealed to 130 K (Fig. 3) and the bands observed when  $\text{CH}_3\text{OH}$  is directly adsorbed at 130 K. Included for comparison are band assignments made for multilayer  $\text{CH}_3\text{OH}$  adsorbed on  $\text{Pd}\{110\}$  (Ref. 15) and  $\text{Rh}\{100\}$  (Ref. 28),  $\text{CH}_3\text{OH}$  contained in an Ar matrix (Ref. 37), and the  $\alpha$  phase of crystalline  $\text{CH}_3\text{OH}$  (Ref. 39).

Band assignment	Multilayer $\text{CH}_3\text{OH}/\text{HOPG}$ at 97 K	Annealed multilayer $\text{CH}_3\text{OH}/\text{HOPG}$ or $\text{CH}_3\text{OH}$ adsorbed at 130 K	Multilayer $\text{CH}_3\text{OH}/\text{Pd}\{110\}$ <sup>a</sup>	Multilayer $\text{CH}_3\text{OH}/\text{Rh}\{100\}$ <sup>b</sup>	$\text{CH}_3\text{OH}$ in an Ar matrix <sup>c</sup>	$\alpha$ phase of crystalline $\text{CH}_3\text{OH}$ <sup>d</sup>
$\nu(\text{O-H})$	3260	3290 3174	3301 3193	3245	3667	3284 3187
$\nu_a(\text{CH}_3)$	2983 2956	2983 2958	2987 2959	2980	3006 2962	2982 2955 2912
$2\delta_a(\text{CH}_3)a'$	2956	2958	2959		2956	
$2\delta_a(\text{CH}_3)a''$	2908	2904			2921	
$\nu_s(\text{CH}_3)$	2833	2833	2832	2905	2848	2829
$2\nu(\text{C-O})$		2037	2035		2054	2040
$\delta_s(\text{CH}_3)$	1468	1475	1473	1475	1466 1452	1458 1426
$\delta(\text{COH})$		1521 1475	1516		1334	1514 1470
$\rho(\text{CH}_3)$	1132	1145	1144	1180	1145 1077	1256 1162 1142
$\nu(\text{C-O})$	1045	1037 1027	1028	1040	1034 1028	1046 1029

<sup>a</sup>Reference 15.

<sup>b</sup>Reference 28.

<sup>c</sup>Reference 37.

<sup>d</sup>Reference 39.



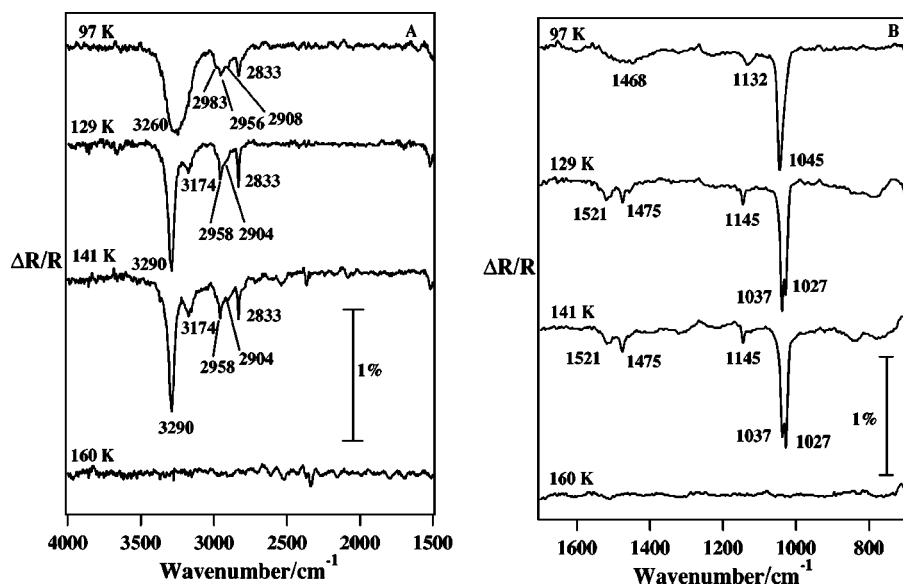


FIG. 3. RAIR spectra resulting from annealing a  $\text{CH}_3\text{OH}$  adlayer adsorbed on HOPG at 97 K. The temperatures to which the adlayer was annealed are shown on the figure. A shows the high frequency region of the spectrum, and B shows the lower frequency region of the spectrum.

phase frequency as previously observed for condensed  $\text{CH}_3\text{OH}$  phases which show hydrogen bonding.<sup>15,39</sup>

Figure 3 shows a series of spectra that result from annealing an overlayer produced by adsorbing 50 L of  $\text{CH}_3\text{OH}$  on HOPG at 97 K. It can clearly be seen that annealing the  $\text{CH}_3\text{OH}$  overlayer to 129 K immediately leads to the splitting of several of the bands observed in the spectrum. The O–H stretch, seen at  $3260\text{ cm}^{-1}$ , splits into two bands at  $3290$  and  $3174\text{ cm}^{-1}$ . Although these bands are sharper than the original band, they are still quite broad and appear to be superimposed on a broad background, perhaps suggesting that the feature originally observed at  $3260\text{ cm}^{-1}$  still remains in the spectrum. The C–O stretch, originally observed at  $1045\text{ cm}^{-1}$ , also splits on heating to give two bands at  $1037$  and  $1027\text{ cm}^{-1}$ . The broad band originally observed at  $1468\text{ cm}^{-1}$ , assigned to the asymmetric  $\text{CH}_3$  stretch, splits on heating to give bands at  $1521$  and  $1475\text{ cm}^{-1}$ . In addition to the splitting of these bands, other bands in the spectrum sharpen on annealing and the band originally observed at  $1132\text{ cm}^{-1}$  sharpens and shifts to  $1145\text{ cm}^{-1}$ . All of the infrared bands have disappeared from the spectra shown in Fig. 3 by 160 K, implying that the  $\text{CH}_3\text{OH}$  has desorbed from the surface by this temperature. This desorption temperature is in good agreement with observations of the adsorption of multilayer  $\text{CH}_3\text{OH}$  on  $\text{Ru}\{001\}$  where the physisorbed multilayer desorbed by 190 K.<sup>25</sup>

The splitting of bands, observed when a  $\text{CH}_3\text{OH}$  overlayer adsorbed at 97 K is annealed, can be attributed to the formation of crystalline  $\text{CH}_3\text{OH}$  on the HOPG surface. The same effect has been observed for multilayers of  $\text{CH}_3\text{OH}$  adsorbed on  $\text{Ru}\{001\}$ ,<sup>25</sup> polycrystalline Pt,<sup>32</sup>  $\text{Pt}\{111\}$ ,<sup>34</sup>  $\text{Rh}\{100\}$ ,<sup>28</sup>  $\text{Pd}\{100\}$ ,<sup>22</sup>  $\text{Pd}\{110\}$ ,<sup>15</sup> and  $\text{Cu}\{110\}$ .<sup>35</sup> Crystalline  $\text{CH}_3\text{OH}$  exists in hydrogen bonded chains in two distinct phases: the  $\alpha$  and  $\beta$  phases.<sup>40–43</sup> Experiments have indicated that the  $\alpha$  phase is stable below 156 K and the  $\beta$  phase is stable between 156 K and the melting point of  $\text{CH}_3\text{OH}$  at 175 K.<sup>44</sup> The two forms of crystalline  $\text{CH}_3\text{OH}$  differ in the distribution of the methyl group above and below the O atoms in the crystalline chains. For the  $\alpha$  chains, the methyl

groups alternate above and below the O atoms allowing neighboring chains to pack closely together. In the  $\beta$  form, the methyl groups are randomly distributed.<sup>45</sup> For the  $\alpha$  and  $\beta$  phases, coupling can take place between vibrations within individual chains (intrachain coupling) and for the  $\alpha$  phase coupling can also occur between adjacent chains (interchain coupling).<sup>15</sup> This leads to the observed splitting in the C–O and O–H stretches.<sup>39,45</sup>

The assignments of the bands observed in Fig. 3, following annealing of a  $\text{CH}_3\text{OH}$  multilayer formed at 97 K, are given in Table I. The frequencies of the observed vibrations show excellent agreement with those previously measured for the  $\alpha$  phase of crystalline  $\text{CH}_3\text{OH}$ .<sup>39</sup> However, it is not possible to conclusively determine whether the crystalline  $\text{CH}_3\text{OH}$  formed on HOPG adopts the  $\alpha$  or  $\beta$  phase, as the vibrational structure of the two phases has not yet been fully resolved.<sup>40,42</sup> It is also not clear from the spectra shown in Fig. 3 whether the whole multilayer is converted to crystalline  $\text{CH}_3\text{OH}$ . In fact the bands at  $3290$  and  $3174\text{ cm}^{-1}$ , which are attributed to the O–H stretch, appear to be superimposed on a broader, less intense, band suggesting that incomplete conversion of the disordered multilayer to the crystalline phase takes place. Further information concerning the conversion of disordered  $\text{CH}_3\text{OH}$  to crystalline  $\text{CH}_3\text{OH}$  was obtained from the TPD data and will be discussed later.

In addition to the observed temperature dependence, experiments also showed that the formation of crystalline  $\text{CH}_3\text{OH}$  is coverage dependant. If a multilayer that results from an exposure of 20 L of  $\text{CH}_3\text{OH}$  is annealed, no splitting of bands is observed and the overlayer that is formed simply desorbs from the surface between 150 and 160 K. However, when an overlayer resulting from a  $\text{CH}_3\text{OH}$  dose of  $\geq 50$  L is annealed, splitting is observed in the infrared spectrum and crystalline  $\text{CH}_3\text{OH}$  is formed. This is in good agreement with previous observations which showed that a minimum exposure was required before the formation of crystalline  $\text{CH}_3\text{OH}$  could be observed.<sup>22,25,28,32,34,35</sup>

Since the observation of the formation of crystalline  $\text{CH}_3\text{OH}$  was also temperature dependent, additional adsorp-

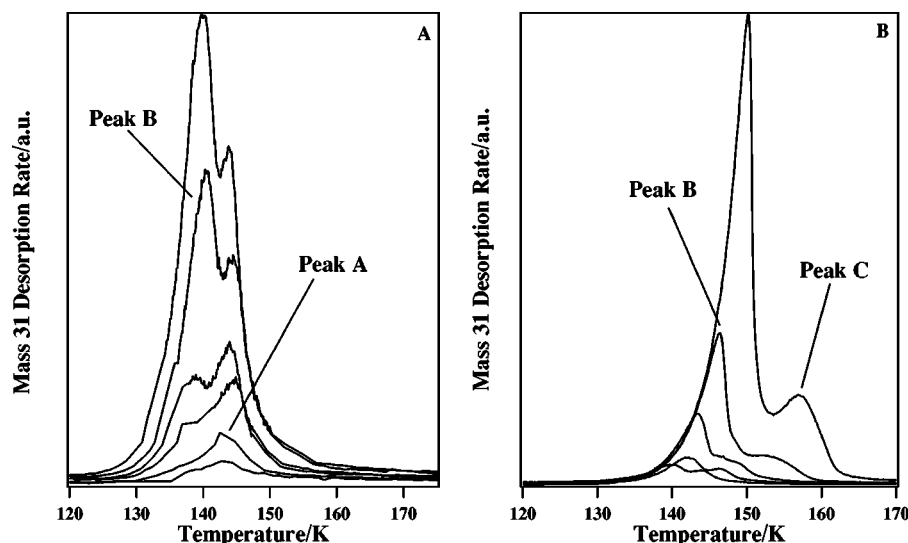


FIG. 4. TPD spectra recorded following various exposures of  $\text{CH}_3\text{OH}$  to the HOPG surface at 105 K. A shows TPD spectra following low  $\text{CH}_3\text{OH}$  exposures of 2, 3, 5, 7, 10, and 15 L. B shows spectra recorded following higher  $\text{CH}_3\text{OH}$  exposures of 15, 20, 50, 100, and 300 L.

tion experiments were performed with the surface held at 130 K. RAIR spectra were recorded as a function of increasing  $\text{CH}_3\text{OH}$  exposure. Initial adsorption of  $\text{CH}_3\text{OH}$  at lower exposures ( $< 50$  L) led to essentially identical spectra to those recorded following adsorption at 97 K (Fig. 1). The intensities of all of the vibrational bands were slightly lower for adsorption at 130 K, compared to 97 K, due to a lower sticking probability at the higher temperature. However, increasing exposures of  $\text{CH}_3\text{OH}$  ( $\geq 100$  L) at 130 K show distinct differences compared to spectra recorded following adsorption at 97 K. Higher exposures produce spectra which are basically identical to those recorded following annealing of the adlayer formed at 97 K, with band splitting occurring in the C–O and O–H stretching modes. Splitting could only be observed for doses of  $\text{CH}_3\text{OH} \geq 100$  L. Annealing the adlayer formed following  $\text{CH}_3\text{OH}$  exposure to HOPG at 130 K did not lead to the formation of any new spectral features and all vibrational bands disappeared from the spectrum by 160 K, similar to adsorption at 97 K.

## B. TPD experiments

### 1. Results

TPD spectra were recorded following  $\text{CH}_3\text{OH}$  adsorption on HOPG at 105 and 130 K. All spectra were recorded with a linear heating rate of  $0.5 \text{ K s}^{-1}$ . Spectra are shown with desorption peaks for mass 31 only. Mass 31 is the major fragment ion created in the mass spectrometer when detecting  $\text{CH}_3\text{OH}$ , and is not the result of any surface chemistry. To confirm this, the ratio of mass 32 desorption to mass 31 desorption was checked regularly and compared with the cracking pattern of  $\text{CH}_3\text{OH}$  recorded with the same mass spectrometer when  $\text{CH}_3\text{OH}$  was dosed into the UHV chamber. In all cases the ratio of mass 32 desorption to mass 31 desorption was 0.73.

A series of TPD spectra, recorded following the adsorption of  $\text{CH}_3\text{OH}$  on HOPG at 105 K, are shown in Fig. 4. Following the lowest exposures of  $\text{CH}_3\text{OH}$  (2 and 3 L) only one peak is observed with a desorption temperature of  $\sim 144$  K. This is labeled as peak A. As the exposure is increased to 5 L a second, lower temperature, peak is observed,

initially as a shoulder on peak A. Following an exposure of 7 L, this shoulder can be clearly identified as a separate peak at  $\sim 139$  K. This peak is labeled as peak B. As the exposure is further increased to 10 and 15 L, peak B begins to dominate the spectrum. The desorption temperature of peak B also increases with increasing  $\text{CH}_3\text{OH}$  exposure. Figure 4(b) shows TPD spectra following higher exposures of  $\text{CH}_3\text{OH}$  to the surface. It is clear that, with increasing exposure, peaks A and B merge into one and the resulting peak continues to grow and shift up in temperature. As the exposure is increased above 50 L, an additional peak (peak C) is observed at around 157 K. Increasing exposure causes peak C to grow in intensity and shift up in temperature. Peaks B and C cannot be saturated.

Peak A is assigned to the desorption of  $\text{CH}_3\text{OH}$  from a physisorbed monolayer adsorbed on the HOPG surface. This peak is the first to appear in the spectrum and hence must be due to  $\text{CH}_3\text{OH}$  that is closely associated with the surface. Peaks B and C are assigned to the desorption of multilayer  $\text{CH}_3\text{OH}$  from the HOPG surface. It is noted that the desorption of multilayers should be a zero-order process and that the resulting TPD spectra should therefore share a leading edge. However, it is clear from Figs. 4(a) and 4(b) that the spectra do not share a leading edge, suggesting a fractional order desorption process as previously observed for  $\text{CH}_3\text{OH}$  adsorbed on  $\text{Pd}\{100\}$ ,<sup>22</sup>  $\text{NiO}$ ,<sup>36</sup> and  $\text{Al}_2\text{O}_3$ .<sup>46</sup> This point will be discussed in more detail later.

As RAIR spectra recorded following  $\text{CH}_3\text{OH}$  adsorption at 130 K showed distinct differences compared to those recorded for 97 K adsorption, TPD spectra were also recorded following higher temperature adsorption. Figure 5 shows TPD spectra recorded following  $\text{CH}_3\text{OH}$  adsorption on HOPG at 130 K. The spectra seen in Fig. 5 are very similar to those in Fig. 4, with a few small differences. Hence, the species giving rise to the three desorption peaks observed in Fig. 5 are assigned to the same species as observed following adsorption at 105 K. The first difference between the spectra in Fig. 5 and those in Fig. 4 is that peak B is observed to grow into the spectrum at slightly higher exposures when  $\text{CH}_3\text{OH}$  is adsorbed at 130 K. This is due to a lower sticking

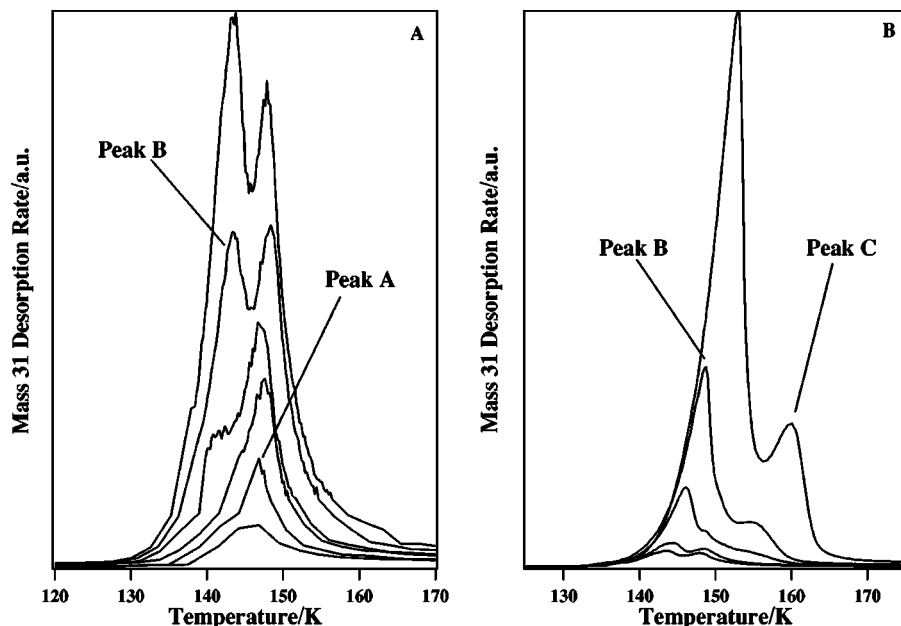


FIG. 5. TPD spectra recorded following various exposures of  $\text{CH}_3\text{OH}$  to the HOPG surface at 130 K. *A* shows TPD spectra following low  $\text{CH}_3\text{OH}$  exposures of 2, 3, 5, 7, 10, and 15 L. *B* shows spectra recorded following higher  $\text{CH}_3\text{OH}$  exposures of 15, 20, 50, 100, and 300 L.

probability at the higher adsorption temperature. The desorption temperatures for the peaks seen in Fig. 5 are also a few degrees higher than those observed following adsorption at 105 K. This could be due to differing amounts of hydrogen bonding in the overlayers formed at 105 and 130 K. This is supported by the RAIR spectra recorded following adsorption at 130 K, which show a slightly higher vibrational frequency for the O–H stretch, which is very sensitive to the amount of hydrogen bonding present in the system. The final difference between the spectra in Fig. 5 and those in Fig. 4, is the more pronounced nature of peak *C* following adsorption at 130 K [Fig. 5(b)] compared to adsorption at 105 K [Fig. 4(b)]. This will be discussed in more detail later.

## 2. Peak fitting

In order to obtain quantitative information about the desorption of  $\text{CH}_3\text{OH}$  from the HOPG surface, it is necessary to separate the TPD spectra into individual peaks so that the contributions from different desorbing species can be evaluated. This requires that the recorded TPD spectra are peak fitted. The package used to fit the experimental data was IGOR Pro (version 5.00, Wavemetrics Inc.). A Lorentzian peak shape was chosen to fit the data as this gave the smallest chi squared value for individual fits, and hence the most accurate overall fit. Since the baselines of the TPD spectra were not perfectly flat, the baseline was also fitted with a cubic polynomial function. For all of the data, the number of peaks used in the fit reflected the actual number of peaks observed in the TPD spectrum. Hence, for the 2 and 3 L spectra only one peak is used for the fit (peak *A*), while two peaks are used to fit the spectra recorded following  $\text{CH}_3\text{OH}$  exposures of 5–20 L (peaks *A* and *B*). For exposures of 50 L and above it was not possible to distinguish peaks *A* and *B* and therefore two peaks were used to fit these spectra: peaks *A/B* and peak *C*. The error introduced by neglecting peak *A* at higher exposures is small as, at these exposures, peak *A* comprises only around 3% of the total peak area. For both

105 and 130 K adsorption, two sets of data were fitted and analyzed to both check the reproducibility of the results and to check the quality of the fitting procedure. Figure 6 shows an example of a fit to the TPD data recorded following a 15 L exposure of  $\text{CH}_3\text{OH}$  to the HOPG surface at 105 K. It is clear from Fig. 6 that the quality of the fit is very good. It was possible to achieve fits of the same quality for all spectra recorded following dosing at both 105 and 130 K.

To further determine the accuracy of the peak fitting procedure, certain key features such as the peak area and peak temperature of the measured and fitted TPD curves were calculated and compared. Peak temperatures were found to be in good agreement between the measured and fitted data. Figure 7 shows a comparison of the integrated area as a function of exposure for measured and fitted TPD data resulting from  $\text{CH}_3\text{OH}$  adsorption at 105 K on the HOPG surface. It is clear that the agreement between the two sets of integrated areas is good.

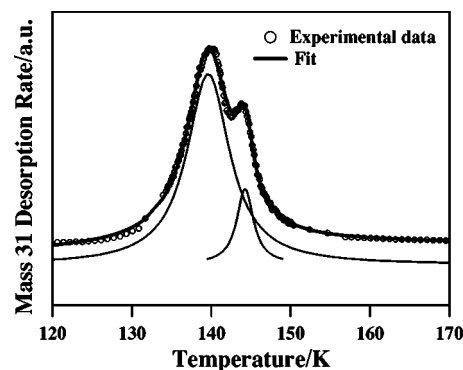


FIG. 6. Figure showing an example of a peak fit to experimental data recorded following a  $\text{CH}_3\text{OH}$  exposure of 15 L to the HOPG surface at 105 K. The TPD spectrum has been fitted with two baseline corrected Lorentzian functions. The dots represent the experimental data, the thin lines represent the individual Lorentzian functions, and the thick line shows the total combined fit to the experimental data.



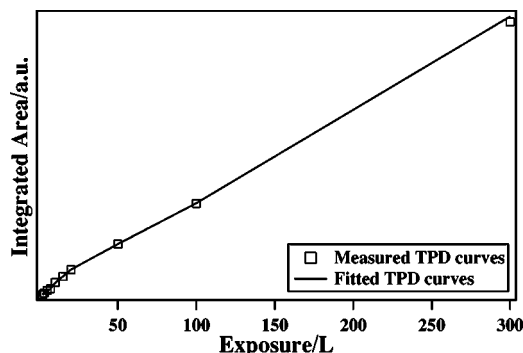


FIG. 7. Graph showing the integrated area, as a function of  $\text{CH}_3\text{OH}$  exposure, of the experimentally measured and fitted TPD curves obtained following  $\text{CH}_3\text{OH}$  adsorption on HOPG at 105 K. Good agreement is obtained between the areas calculated for both sets of data. This graph also shows that the sticking probability of  $\text{CH}_3\text{OH}$  on the HOPG surface is approximately constant over the whole exposure range.

### 3. Uptake curves

Figure 7 shows the total uptake of  $\text{CH}_3\text{OH}$  on the HOPG surface at 105 K as a function of increasing  $\text{CH}_3\text{OH}$  exposure. It is clear that the uptake of  $\text{CH}_3\text{OH}$  is fairly linear, implying a constant sticking probability as a function of exposure. This is characteristic of physisorption. As well as determining the total uptake of  $\text{CH}_3\text{OH}$ , it was also possible to determine the relative coverage of each desorbing species as a function of exposure, once a good fit to the measured TPD data had been achieved. The relative coverage for each species was evaluated by integrating the area under the individual TPD peaks produced from the peak fitting procedure. It was only possible to determine relative coverage and not absolute coverage as our current experimental setup does not allow a measurement of the actual coverage on the surface.

Figure 8 shows the integrated areas of peaks A, B, and C as a function of exposure following adsorption at 105 K. The data shown are the average of two sets of data. Similar curves, showing virtually identical trends, can also be produced for data recorded following adsorption at 130 K. It is

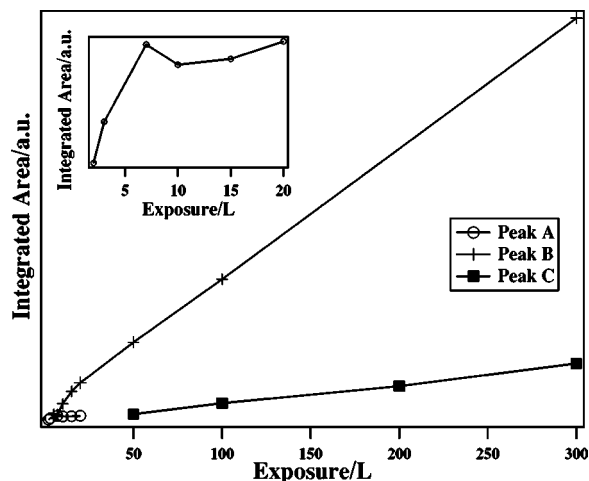


FIG. 8. Graph showing the integrated areas of the individual peaks that make up the TPD spectra recorded following  $\text{CH}_3\text{OH}$  adsorption on HOPG at 105 K. The inset shows a close up of the data for peak A, the monolayer peak.

clear from Fig. 8 that the relative coverage of the species giving rise to peaks B and C increases fairly linearly with exposure and does not saturate. This confirms the assignment of these peaks to the desorption of multilayer  $\text{CH}_3\text{OH}$  from the surface. The exact nature of the multilayer species giving rise to peaks B and C is discussed in more detail later. The inset in Fig. 8 shows a close up of the integrated area of peak A as a function of increasing  $\text{CH}_3\text{OH}$  exposure. It is clear that the area of peak A increases as the exposure is increased from 2 to 7 L, indicating that the relative coverage of this species on the surface also increases. However, for exposures of 10 L and above, the integrated area of peak A saturates. This confirms the assignment of this peak to the desorption of a monolayer of  $\text{CH}_3\text{OH}$  from the HOPG surface. The fact that the desorption of monolayer  $\text{CH}_3\text{OH}$  can be distinguished from multilayer  $\text{CH}_3\text{OH}$  indicates that, although weak, the bonding between  $\text{CH}_3\text{OH}$  and the surface is slightly stronger than the bonding between two  $\text{CH}_3\text{OH}$  molecules that occurs in the multilayer. The same effects are also seen following adsorption at 130 K. However, peak A is observed to saturate at a slightly higher exposure due to the lower sticking probability at the higher adsorption temperature. The monolayer saturation coverage is, however, similar for adsorption at 105 and 130 K as the integrated area under peak A saturates at approximately the same value in both cases.

Figure 8 also shows that multilayers of  $\text{CH}_3\text{OH}$  on the HOPG surface begin to grow even before the monolayer is saturated, as peak B becomes populated before peak A saturates. This effect has previously been observed for  $\text{CH}_3\text{OH}$  adsorbed on HOPG<sup>8</sup> and also on  $\text{NiO}$ <sup>36</sup> and  $\text{Al}_2\text{O}_3$ .<sup>46</sup> This observation further suggests that the desorption of  $\text{CH}_3\text{OH}$  multilayers from the HOPG surface is not a perfect zero-order process. Multilayers which desorb with zero-order kinetics are seen to adsorb and desorb in a layer-by-layer fashion which is clearly not the case here. Since the bonding of  $\text{CH}_3\text{OH}$  to the HOPG surface is observed to be slightly stronger than that of  $\text{CH}_3\text{OH}$  to another  $\text{CH}_3\text{OH}$  molecule, it is assumed that this “islanding” of molecules occurs due to a lack of mobility at this adsorption temperature, rather than due to an energetic effect.

### 4. Desorption orders

In order to gain a deeper understanding of the desorption kinetics for  $\text{CH}_3\text{OH}$  adsorbed on HOPG, the desorption order for each of the individual desorbing species has been determined. Thermal desorption is described by the Polanyi–Wigner equation:<sup>47–49</sup>

$$r_{\text{des}} = -\frac{d\theta}{dt} = v_n \theta^n \exp\left(\frac{-E_{\text{des}}}{RT}\right), \quad (1)$$

where  $r_{\text{des}}$  is the rate of desorption,  $v_n$  is the preexponential factor for the desorption process of order  $n$ ,  $\theta$  is the coverage,  $E_{\text{des}}$  is the desorption activation energy,  $R$  is the gas constant, and  $T$  is the surface temperature. The rate of change of coverage  $\theta$  with time  $t$  can be linked to the rate of change of coverage with temperature via the TPD heating rate  $\beta$ ,

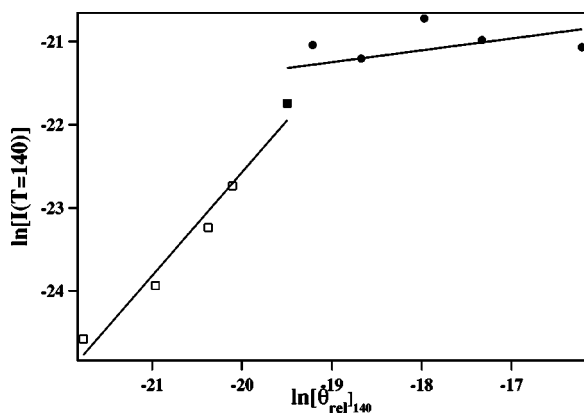


FIG. 9. A plot of  $\ln[I(T=140)]$  against  $\ln[\theta_{\text{rel}}]_{140}$  for the data shown in Fig. 4. This graph allows the order of desorption to be determined from the gradient of the plot. The open squares represent the data for exposures between 2 and 10 L (the monolayer) and the filled circles are for exposures of 15 L and above (the multilayer).

$$\frac{d\theta}{dt} = \frac{d\theta}{dT} \times \frac{dT}{dt} = \frac{d\theta}{dT} \beta. \quad (2)$$

In TPD experiments, the rate of change of coverage with temperature is proportional to the intensity of the measured TPD trace  $I(T)$ . In the experiments described here it is not possible to measure an absolute coverage, however integrating the area under the TPD peaks does allow a relative coverage  $\theta_{\text{rel}}$ , to be obtained. Hence Eq. (1) can now be rewritten as

$$I(T) \propto v_n \theta_{\text{rel}}^n \exp\left(\frac{-E_{\text{des}}}{RT}\right). \quad (3)$$

Taking logarithms of both sides of this equation leads to Eq. (4)

$$\ln[I(T)] \propto n \ln[v_n \theta_{\text{rel}}] - \frac{E_{\text{des}}}{RT}. \quad (4)$$

At a fixed temperature, here defined as  $T_x$ , Eq. (4) shows that the order of desorption can be determined by performing a plot of  $\ln[I(T_x)]$  against  $\ln[\theta_{\text{rel}}]_{T_x}$ . The gradient of this graph will give  $n$ , the order of desorption.<sup>48</sup> Note that in order to perform this plot it is necessary to assume that the preexponential factor and the desorption energy do not vary with coverage or with temperature. This is a good assumption for the preexponential factor, as all of the  $\text{CH}_3\text{OH}$  is physisorbed on the surface. This is also an acceptable assumption for the desorption energy which shows only a weak variation with coverage (see later).

Figure 9 shows a plot of  $\ln[I(T_x)]$  against  $\ln[\theta_{\text{rel}}]_{T_x}$  for a  $T_x$  value of 140 K for  $\text{CH}_3\text{OH}$  adsorption on HOPG at 105 K. This value of  $T_x$  was chosen to ensure that sufficient intensity in both the monolayer peak (peak A) and the multilayer peak (peak B) could be obtained with increasing exposure. Note that this plot was produced directly from the experimental data and not from the fitted TPD data. It is obvious from Fig. 9 that there is a different gradient in this plot for exposures  $\leq 10$  L (open squares) and for exposures above 10 L (filled circles). The reason for this can clearly be seen by looking at Fig. 4 which shows that for the lower

TABLE II. Table showing the calculated order of desorption for the monolayer and multilayer peaks (peaks A and B) observed in the TPD spectra that result from the exposure of the HOPG surface to  $\text{CH}_3\text{OH}$ . The numbers given in the table are the average values obtained from analyzing four separate sets of data. The order of desorption  $n$  is obtained from the gradient of a plot of  $\ln[I(T_x)]$  against  $\ln[\theta_{\text{rel}}]_{T_x}$  at a fixed temperature  $T_x$ . An example of such a plot is shown in Fig. 9.

$T_x$ (K)	$n$ for peak A (monolayer)	$n$ for peak B (multilayer)
140	1.28	0.17
142.5	1.09	0.46
145	1.31	0.41

exposures ( $< 10$  L) the chosen  $T_x$  value passes through peak A (the monolayer peak), while for exposures above 10 L the chosen  $T_x$  value passes through peak B (the multilayer peak). Figure 9 therefore shows that, as expected, the order of desorption is different for monolayer and multilayer  $\text{CH}_3\text{OH}$ . The gradients of the graph shown in Fig. 9 give a desorption order of 1.24 for peak A (the monolayer peak) and 0.14 for peak B (the multilayer peak). In order to check the accuracy of these values, this process was repeated for a variety of fixed temperatures  $T_x$  and for a range of TPD data sets. The gradients of the resulting graphs, and hence the desorption orders for the monolayer and multilayer peaks, are given in Table II. The data in Table II are the average desorption orders that result from the analysis of four sets of TPD data recorded following adsorption at both 105 and 130 K.

Analysis of all  $T_x$  values shows that peak A has a desorption order of  $1.23 \pm 0.14$ , again confirming its assignment to the desorption of monolayer  $\text{CH}_3\text{OH}$ . Since  $\text{CH}_3\text{OH}$  has been shown to adsorb reversibly on HOPG, first-order desorption would be expected and a desorption order of one has previously been used to model  $\text{CH}_3\text{OH}$  desorption from a monolayer adsorbed on  $\text{Al}_2\text{O}_3$ .<sup>46</sup> A first-order desorption process assumes that each desorbing molecule is not influenced by surrounding molecules on the surface. The value of  $1.23 \pm 0.14$ , determined here for monolayer  $\text{CH}_3\text{OH}$  desorption from HOPG, is slightly higher than the expected value of 1. This can be attributed to interactions, such as hydrogen bonding, that occur within the monolayer. Peak B has a calculated desorption order of  $0.35 \pm 0.21$ , in excellent agreement with other studies which have shown that multilayer  $\text{CH}_3\text{OH}$  desorption is a fractional order process.<sup>22,36,46</sup> The observation of a fractional desorption order for multilayer  $\text{CH}_3\text{OH}$  desorption from HOPG is supported by the fact that TPD spectra for increasing doses of  $\text{CH}_3\text{OH}$  (seen in Figs. 4 and 5) do not share leading edges as would be expected for perfect zero-order desorption. The observed fractional order desorption for peak B (the multilayer peak) is assigned to the presence of hydrogen bonding in the  $\text{CH}_3\text{OH}$  multilayer that leads to strong interactions between adjacent molecules. The infrared spectra (shown in Fig. 1) also show evidence of strong hydrogen bonding as shown by the vibrational frequency and broadness of the O–H stretching band. Note that desorption orders have not been calculated for the second multilayer species that gives rise to peak C. This is because this peak only appears in the spectra at relatively high

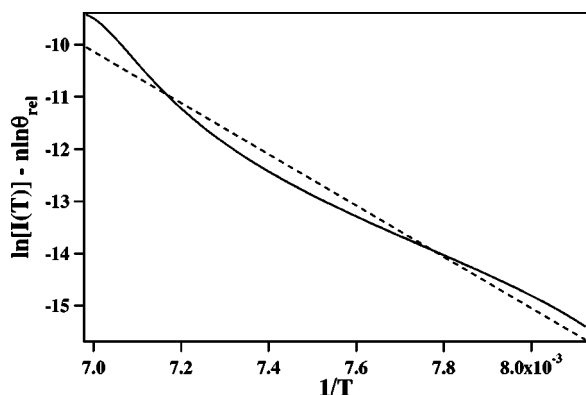


FIG. 10. A graph of  $(\ln[I(T)] - n \ln \theta_{\text{rel}})$  against  $1/T$  for a multilayer of  $\text{CH}_3\text{OH}$  adsorbed on HOPG following a 50 L exposure at 105 K. This graph was plotted with a desorption order of 0.35. The gradient of the graph is equal to  $-E_{\text{des}}/R$  and allows a value for the desorption energy to be obtained. The solid line shows the actual data points and the dashed line shows a fit to this data that allows the gradient to be determined.

$\text{CH}_3\text{OH}$  doses and therefore there is only a small amount of data for this peak. In addition, it is thought that this TPD peak partially arises due to the heating process in the TPD experiment (see later).

### 5. Desorption energies

As well as obtaining the order of desorption, it is also possible to determine the desorption energy for  $\text{CH}_3\text{OH}$  adsorbed on HOPG. This gives an indication of the strength of the binding of  $\text{CH}_3\text{OH}$ , both to the HOPG surface and within the multilayer.

Equation (4) can be rewritten as follows:

$$\ln[I(T)] \propto n \ln v_n + n \ln \theta_{\text{rel}} - \frac{E_{\text{des}}}{RT}. \quad (5)$$

Further rearrangement then gives Eq. (6):

$$\ln[I(T)] - n \ln \theta_{\text{rel}} \propto n \ln v_n - \frac{E_{\text{des}}}{RT}. \quad (6)$$

Hence plotting  $(\ln[I(T)] - n \ln \theta_{\text{rel}})$  against  $1/T$  should give a straight line with a gradient of  $-E_{\text{des}}/R$ . Again this assumes that the preexponential factor is constant, a good assumption given that  $\text{CH}_3\text{OH}$  is physisorbed on HOPG at all coverages. Note that the intercept cannot be used to give a value for the preexponential factor  $v_n$  as the coverage is only a relative coverage. In order to obtain a value for  $v_n$  from a plot of this type, it is necessary to know the absolute coverage.

Figure 10 shows a plot of  $(\ln[I(T)] - n \ln \theta_{\text{rel}})$  against  $1/T$  for the multilayer, following a 50 L exposure of  $\text{CH}_3\text{OH}$  to HOPG at 105 K. Note that in order to plot this graph, it was necessary to separate out the contributions of the different TPD peaks (A, B, and C) and hence this plot is performed for the peak fitted TPD data not the raw data. Similar plots were performed for both the monolayer species (peak A) and the multilayer species (peak B) using the range of  $n$  values already determined. These plots were performed for several sets of TPD data, in order to obtain average values for the desorption energies.

Figure 11 shows how the calculated desorption energy

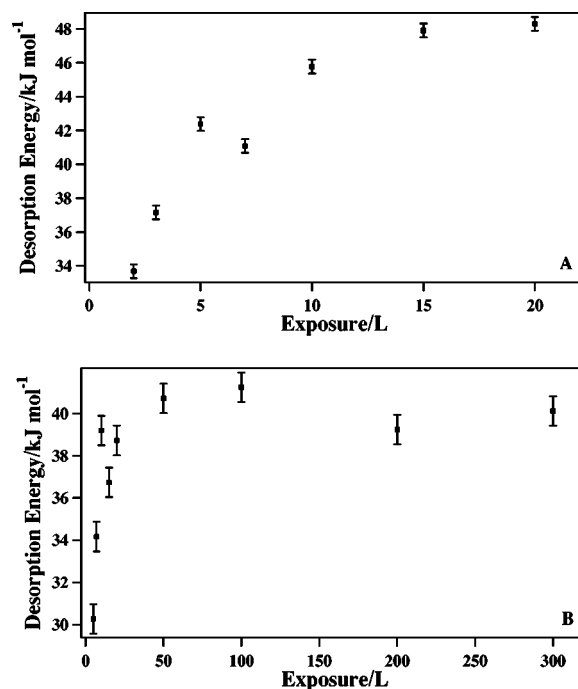


FIG. 11. Graphs showing the variation of the desorption energy of  $\text{CH}_3\text{OH}$  on the HOPG surface for A the monolayer and B the multilayer as a function of exposure at 105 K. The data points represent the average desorption energy calculated from several sets of TPD data. The error bars represent the error that arises from the uncertainty in the value of the desorption order  $n$ .

for both the monolayer [Fig. 11(a)] and the multilayer [Fig. 11(b)] vary as a function of  $\text{CH}_3\text{OH}$  exposure on HOPG at 105 K. The data points represent the average desorption energy calculated from several sets of TPD data, and the error bars represent the error in the calculated desorption energy that arises from the uncertainty in the value of the desorption order  $n$ . Data for 130 K adsorption are not shown here but show very similar results. As for the desorption orders, no value of the desorption energy has been calculated for peak C. Figure 11(a) shows that the desorption energy for the monolayer (peak A) increases from  $\approx 33$  to  $48 \text{ kJ mol}^{-1}$  as the  $\text{CH}_3\text{OH}$  exposure increases from 2 to 20 L. This desorption energy corresponds either to a strongly physisorbed species or to a weakly chemisorbed species. However, the RAIR spectra also recorded for this adsorption system suggest that chemisorbed  $\text{CH}_3\text{OH}$  is not adsorbed on the HOPG surface and hence it is assumed that the  $\text{CH}_3\text{OH}$  monolayer is, instead, strongly physisorbed. The observed increase in desorption energy with increasing exposure indicates that the  $\text{CH}_3\text{OH}$  becomes more strongly bound as the coverage increases. It is most likely that this is due to increasing amounts of hydrogen bonding between the  $\text{CH}_3\text{OH}$  molecules that becomes possible as the coverage increases.

Figure 11(b) shows the desorption energy for the multilayer peak, peak B, as a function of increasing  $\text{CH}_3\text{OH}$  exposure. It is clear that the multilayer desorption energy also increases with increasing coverage from  $31 \text{ kJ mol}^{-1}$  up to around  $40 \text{ kJ mol}^{-1}$  following a 300 L  $\text{CH}_3\text{OH}$  exposure. Again this corresponds to the desorption of a physisorbed species and is in good agreement with desorption energies of 30.2 and  $37.7 \text{ kJ mol}^{-1}$  previously reported for two phys-

isorbed states of  $\text{CH}_3\text{OH}$  desorbing from  $\text{Pd}\{100\}$ .<sup>22</sup> This desorption energy is also in good agreement with the enthalpy of sublimation of  $\text{CH}_3\text{OH}$  which is  $44.9 \text{ kJ mol}^{-1}$ .<sup>46</sup> It is noted that, as expected, at all  $\text{CH}_3\text{OH}$  exposures the calculated desorption energy is larger for the monolayer than for the multilayer. As for the monolayer, it is assumed that the observed increase in the desorption energy with increasing coverage can be assigned to the larger amounts of hydrogen bonding that occur within the multilayer at higher  $\text{CH}_3\text{OH}$  exposures.

The data in Fig. 11(b) suggest two possible regimes for the adsorption of multilayer  $\text{CH}_3\text{OH}$ . Initially, the desorption energy of the multilayer increases rapidly with increasing  $\text{CH}_3\text{OH}$  exposure, but at an exposure above 10–20 L the desorption energy seems to plateau. Previous investigations have suggested the formation of an intermediate or “sandwich” phase of  $\text{CH}_3\text{OH}$ <sup>15</sup> in which the lattice mismatch between bulk  $\text{CH}_3\text{OH}$  ice and the  $\text{CH}_3\text{OH}$  that is bound to the surface is accommodated. It is therefore suggested that it is this intermediate phase of disordered multilayer  $\text{CH}_3\text{OH}$  that shows the rapid increase in desorption energy, due to the formation of increasing amounts of hydrogen bonding as the multilayer grows. The approximately constant desorption energy, observed above  $\text{CH}_3\text{OH}$  doses of 10–20 L, occurs due to the subsequent formation of more ordered  $\text{CH}_3\text{OH}$  overlayers in which the amount of hydrogen bonding remains constant with increasing exposure.

## 6. Model for the adsorption of $\text{CH}_3\text{OH}$ on HOPG

Putting together the data obtained from both RAIRS and TPD allows a model of the adsorption of  $\text{CH}_3\text{OH}$  on HOPG to be developed. RAIRS spectra have shown that  $\text{CH}_3\text{OH}$  is always physisorbed on the HOPG surface and that crystalline  $\text{CH}_3\text{OH}$  can be formed provided the surface temperature and coverage are high enough. TPD data shows that it is possible to distinguish the desorption of monolayer  $\text{CH}_3\text{OH}$  (peak A, Fig. 4) and multilayer  $\text{CH}_3\text{OH}$  (peaks B and C, Fig. 4). Peaks B and C have both been assigned to the desorption of multilayer  $\text{CH}_3\text{OH}$ , however, the difference between these two multilayer species needs to be determined.

A possible assignment for peak C uses information obtained from the RAIRS spectra. As already discussed, the formation of crystalline  $\text{CH}_3\text{OH}$  can be observed with RAIRS either upon annealing the surface after adsorption at 97 K, or following adsorption to high exposures at 130 K. The TPD spectra seen in Figs. 4(b) and 5(b) show that peak C is only observed at  $\text{CH}_3\text{OH}$  exposures  $\geq 50 \text{ L}$  in both the 100 and 130 K TPD spectra. This peak is therefore assigned to the desorption of crystalline multilayer  $\text{CH}_3\text{OH}$ . Note that no crystalline  $\text{CH}_3\text{OH}$  is formed on the surface during adsorption at 105 K, irrespective of exposure. However, during the TPD process some of the  $\text{CH}_3\text{OH}$  multilayer is converted to crystalline  $\text{CH}_3\text{OH}$  which then desorbs as a separate peak. In agreement with the RAIRS data, where crystalline  $\text{CH}_3\text{OH}$  could not be formed for exposures  $< 50 \text{ L}$ , peak C only appears in the TPD spectrum for  $\text{CH}_3\text{OH}$  exposures of 50 L and above.

The assignment of peak C to the formation, and subsequent desorption, of crystalline  $\text{CH}_3\text{OH}$  is supported by the

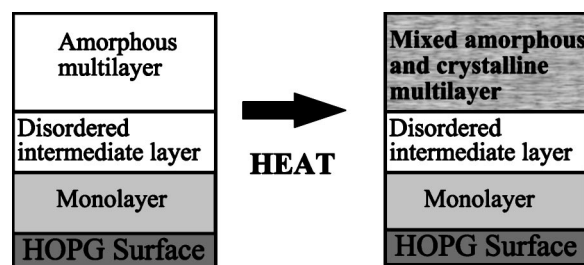


FIG. 12. A schematic diagram showing how  $\text{CH}_3\text{OH}$  is adsorbed on HOPG at 100 K and what happens to the resulting overlayer when heating occurs. The overlayer produced following annealing of an adlayer adsorbed at 100 K is very similar to that produced when  $\text{CH}_3\text{OH}$  is adsorbed at 130 K.

observation that following  $\text{CH}_3\text{OH}$  adsorption at 130 K, the TPD spectra show a more pronounced peak C [Fig. 5(b)]. This arises due to the fact that some crystalline  $\text{CH}_3\text{OH}$  is actually formed during adsorption as well as being formed during the TPD experiment, leading to the desorption of larger amounts of crystalline  $\text{CH}_3\text{OH}$ . Hence, in the TPD spectra shown in Figs. 4 and 5, peak B is assigned to the desorption of disordered, or amorphous, multilayer  $\text{CH}_3\text{OH}$  and peak C is assigned to the desorption of crystalline  $\text{CH}_3\text{OH}$ . It would be expected that crystalline  $\text{CH}_3\text{OH}$  desorbs at a higher temperature than amorphous  $\text{CH}_3\text{OH}$  due to the larger number of hydrogen bonds present in the highly ordered crystalline structure. Note that initial inspection of the RAIRS spectra seen in Fig. 3 suggests that all of the disordered  $\text{CH}_3\text{OH}$  converts to crystalline  $\text{CH}_3\text{OH}$  on annealing, a fact that is clearly in disagreement with the TPD data. However, closer inspection of the RAIRS spectra in Fig. 3 shows that the sharper peaks observed in the O–H region of the spectrum are superimposed on a broad band which is assigned to the presence of disordered  $\text{CH}_3\text{OH}$  multilayers. Therefore it is suggested that disordered and crystalline multilayers coexist on the surface. In addition, annealing in the RAIRS experiments was done in a rather different manner to the heating in the TPD experiments and therefore it is very likely that more  $\text{CH}_3\text{OH}$  could be converted to the crystalline form in the RAIRS experiment compared to in the TPD experiments.

It is now possible to build up a picture of the adsorption of  $\text{CH}_3\text{OH}$  on the HOPG surface and Fig. 12 shows a schematic diagram of this model. When  $\text{CH}_3\text{OH}$  is adsorbed on HOPG at  $\sim 100 \text{ K}$ , initial adsorption leads to the formation of a physisorbed monolayer. Subsequent adsorption leads to the formation of first an intermediate multilayer, and subsequently a disordered, or amorphous, multilayer. These two multilayers cannot be distinguished from one another in the TPD spectrum and both give rise to peak B. Annealing this adlayer (either in a RAIRS experiment or during the TPD experiment) leads to the formation of a mixed crystalline and amorphous overlayer. The crystalline  $\text{CH}_3\text{OH}$  desorbs at a higher temperature than the amorphous  $\text{CH}_3\text{OH}$  due to it having a more ordered structure. Adsorption at 130 K essentially leads to the formation of a  $\text{CH}_3\text{OH}$  adlayer that is very similar to that formed when an adlayer adsorbed at  $\sim 100 \text{ K}$  is annealed, hence accounting for the marked similarity between the TPD data shown in Figs. 4 and 5. Note that the



TPD data show that only around 20%–30% of the CH<sub>3</sub>OH multilayer is converted to crystalline CH<sub>3</sub>OH as peak *C* has an integrated area that is much smaller than that of peak *B*.

Previous work<sup>15</sup> for CH<sub>3</sub>OH adsorbed on Pd{110} has suggested that it is not possible to distinguish between the desorption of amorphous and crystalline CH<sub>3</sub>OH. This is clearly not the case here, however this difference could be due to the different heating rates used in this experiment and the previous experiment.<sup>15</sup> An alternative model was also suggested for the growth of CH<sub>3</sub>OH adlayers on Ag{111}.<sup>33</sup> This model suggested that crystalline CH<sub>3</sub>OH desorbs at a lower temperature than amorphous CH<sub>3</sub>OH.<sup>33</sup> However, this cannot be the case for CH<sub>3</sub>OH desorbing from HOPG as, in this case, peak *B* would be due to the desorption of crystalline CH<sub>3</sub>OH and peak *C* would be due to the desorption of amorphous CH<sub>3</sub>OH. However, peak *B* is observed to appear in the TPD spectra shown in Figs. 4 and 5 following a CH<sub>3</sub>OH exposure of only 7–10 L. This is clearly much lower than the exposure at which the formation of crystalline CH<sub>3</sub>OH is observed with RAIRS and therefore indicates that this alternative model cannot hold for CH<sub>3</sub>OH adsorbed on the HOPG surface.

#### IV. SUMMARY AND CONCLUSIONS

RAIRS and TPD data have shown that CH<sub>3</sub>OH is physisorbed on HOPG at all coverages and that crystalline CH<sub>3</sub>OH can also be formed provided the coverage is high enough. Three desorbing species have been observed with TPD, as a function of increasing exposure, which are assigned to the desorption of a monolayer, an amorphous multilayer, and a crystalline multilayer. The monolayer has a desorption order of  $1.23 \pm 0.14$  and a desorption energy that rises from 33 to 48 kJ mol<sup>-1</sup> with increasing CH<sub>3</sub>OH exposure. The disordered multilayer has a much smaller desorption order of  $0.35 \pm 0.21$  and a desorption energy that also rises as a function of exposure from 31 kJ mol<sup>-1</sup> at low CH<sub>3</sub>OH exposures to  $\sim 40$  kJ mol<sup>-1</sup> at high coverages.

Hydrogen bonding between the CH<sub>3</sub>OH molecules is found to have a strong influence on the behavior of CH<sub>3</sub>OH adsorbed on HOPG. It is thought that it is the presence of hydrogen bonding between adjacent molecules that causes the observed increase in the desorption energy as a function of increasing coverage in both the monolayer and the multilayer. It is also the presence of hydrogen bonding within the overlayer that leads to the observation of a non-zero desorption order for the multilayer. In addition, the multilayer is seen to grow on the HOPG surface even before the monolayer has saturated, again indicating that the formation of hydrogen bonds between the CH<sub>3</sub>OH molecules plays an important role in its adsorption on the HOPG surface. However, at low doses of CH<sub>3</sub>OH on the HOPG surface it is possible to distinguish between the desorption of a monolayer and a multilayer, implying that hydrogen bonding is not always dominant for CH<sub>3</sub>OH adsorption on HOPG. In fact, the binding of the CH<sub>3</sub>OH to the HOPG surface must be slightly stronger than the binding between CH<sub>3</sub>OH molecules in the bulk ice, otherwise it would not be possible to distinguish between monolayer and multilayer adsorption.

The results described here form part of a wider study of the adsorption and formation of a range of astrochemically relevant molecules on dust grain analog surfaces. Whilst the experiments described here were performed at 100 K, as opposed to 10–20 K which is the temperature of dust grains in the ISM, they still provide detailed information about the formation of CH<sub>3</sub>OH ices on grain surfaces and about the subsequent desorption of these ices from the grains. This information is crucially important for astronomical models of the star formation process and the data from this study will be incorporated into suitable astronomical models.<sup>50</sup> Similar TPD results have previously been successfully incorporated into astronomical models<sup>51</sup> of the star formation process.

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